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Magnesium hydroxide whisker modified via in situ copolymerization of n-butyl acrylate and maleic anhydride

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Abstract Magnesium hydroxide (MH) whiskers were modified via in situ polymerization of n-butyl acrylate and maleic anhydride. Sodium dodecyl sulfonate was used as emulsifier. The modifying effect was evaluated by using contact angle and activation index. The thermal stability, functional groups, structure, morphology, phase composition and surface element valence of MH whiskers were characterized by thermogravimetry–differential scanning calorimetry (TG-DSC), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Results reveal that the contact angle and activation index of modified MH whiskers are 105° and 76.5%, the thermal stability shows little change, and the decomposition temperature ranges between 38 and 419 °C. The copolymer of n-butyl acrylate and maleic anhydride absorbed on the surface of MH whiskers leads to the increased diameter and makes the surface of whiskers be rougher. Furthermore, the absorption of element C on the surface of MH whiskers increases, and the diffraction intensity of C 1s spectra increases; thus, the compatibility of whiskers in the organic phase can be improved significantly. Lastly, the surface molecular model of MH whiskers modified via in situ copolymerization of n-butyl acrylate and maleic anhydride is established.

Keywords Magnesium hydroxide whiskers; n-Butyl acrylate; Maleic anhydride; In situ copolymerization; Surface molecular model

1 Introduction

Magnesium hydroxide (MH) whiskers, a kind of functional single crystal with smooth and slim appearance, have attracted considerable attention [1]. MH whiskers are usually used as a filler of polymers to improve their property of reinforcement, flame retardant and smoke suppression, because of their excellent characteristics such as better toughening and reinforcing performances [2, 3]. However, MH whiskers are easy to agglomerate in the preparation and processing for their high surface energy. This property leads to a poor dispersion for MH whiskers in polymer material. Furthermore, the surface of MH whiskers is hydrophilic, which also results in weak combination between MH whiskers and polymer matrix [4–6]. These problems make the composites rarely meet the actual requirement on mechanical properties. Therefore, in order to enhance the compatibility with polymers, the surface modification of MH whiskers is quite important. In recent years, there are an increasing number of studies on the improvement in the compatibility between additive materials and polymer matrix [7, 8]. The activity and coupling agent mostly used in surface modification of additive material have obtained significant effects. The modification

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of MH whiskers has been broadly investigated, and the involved surfactants mainly include silanes, titanates, aluminate esters, etc. [9–12].

In this paper, MH whiskers were modified via in situ copolymerization of n-butyl acrylate and maleic anhydride. The modification effect was characterized by evaluation of wettability. The thermal stability, functional groups, structure, morphology, phase composition and surface element valence of MH whiskers both modified and unmodified were characterized, and the surface molecular model of modification of MH whiskers was established.

2 Experimental

2.1 Preparation of MH whiskers

MH whiskers were prepared via hydrothermal synthesis method using precursor of magnesium oxysulfate (MOS) whiskers and NaOH as reactants. The initial (MOS) whiskers slurry with a concentration of 4 wt% was prepared, and 1.0 mol·L^{-1} NaOH was added to the slurry in the mole ratio of 4.5:1.0(NaOH/MOS). The well-mixed solution was put into the GSH-10 magnetic agitated autoclave under the stirring speed of 100 r·min^{-1}. The reaction was carried out at 180 °C for 4 h. When the reactor cooled down to room temperature at the end of the reaction, the product was dispersed, filtrated and dried.

2.2 Modification of MH whiskers

All chemicals used were of analytical grade (Tian-jin Kemiou Chemical Reagent Co., Ltd.) and used without further purification. Water used was deionized water. 3.75 g n-butyl acrylate and 50 ml sodium dodecyl sulfonate solution (concentration of 15 wt%) were mixed in a three-mouth flask and kept stirring, and 15 g MH whiskers was added gradually. The heating temperature was increased to 60–70 °C, and then, 62.5 ml aqueous solution of maleic anhydride (concentration of 2 wt%) was added slowly within 30 min. The composite was kept reacting for 2 h under the temperature of 85 °C. After the demulsification, the suspended emulsion was washed, filtered and dried. Finally, the modified MH whiskers were obtained.

2.3 Characterization

GB/T16913.5-1997 standard was applied to test the contact angle of MH whiskers. According to the activation index method, 10 g modified MH whiskers was added to 100 ml deionized water under stirring for 2 min and then kept still for a certain time till the solution was clarified. Then, the MH whiskers floating on the surface of the solution were taken out. And the MH whiskers precipitated at the bottom of the beaker were filtered, dried and weighed. The ratio of floating MH whiskers to the total modified MH whiskers used was defined as the activation index. The formula for activation index is shown below:

$$H = \frac{m - m_1}{m} \times 100\% \quad (1)$$

where H (%) stands for activation index, m (g) represents the total mass of MH whiskers added, and m_1 (g) stands for the mass of MH whiskers precipitated at the bottom of the beaker.

Thermal stability of the modified and unmodified MH whiskers products was investigated via thermogravimetry–differential scanning calorimetry (TG-DSC, SDT 2960 TA USA) at a heating rate of 10 °C·min^{-1} under an air atmosphere. The functional groups of the products were analyzed by Fourier transform infrared spectroscopy (FTIR, 380, Nicolet Company). The phase compositions of the products were analyzed by X-ray diffractometer (XRD, Ultima IV, Rigaku, Japan, 40 mA, 40 kV) with Cu Kα radiation at scanning rate of 8 (°)·min^{-1} from 10° to 90°. The wavelength was 1.54056 nm, the stability of current was ±0.03%, and the accuracy of θ was ±0.002°. The morphology of the products was analyzed by scanning electron microscopy (SEM, S-3400N, Hitachi, Japan) at an accelerating voltage of 0.50–30.00 kV, a beam current of 1 pA–1 μA and a resolution of 1.0 nm after the samples were coated with gold. The dried products were examined by X-ray photoelectron spectroscopy (XPS, ESCA-LAB250, Hitachi, Japan) to study the bonding energy of Mg, O, C elements and valence change in whiskers' surface elements with an emitter of Al Kα, power of 150 W (hv = 1486.6 eV, I = 10 mA), spot size of 500 μm, transmission energy of 50 eV and energy step of 0.1 eV.

3 Result and discussion

3.1 Contact angle and activation index of MH whiskers before and after modification

Table 1 shows contact angle and activation index of MH whiskers before and after modification. The MH whiskers modified via in situ polymerization of n-butyl acrylate and maleic anhydride achieve a contact angle of 105° (contact

Table 1 Contact angle and activation index of MH whiskers before and after modification

Types of MH	Contact angle/(°)	Activation index/%
MH before modification	1.30	0.16
MH after modification	105.00	76.50

angle before modification is 1.30°) and an activation index of 76.5% (activation index before modification is 0.16%). Obviously, the modification has a significant impact on MH whiskers.

3.2 TG-DSC analysis of MH whiskers before and after modification

TG-DSC curves for MH whiskers before and after modification are shown in Fig. 1. As seen in Fig. 1, compared with unmodified MH whiskers, modified MH whiskers have decomposition temperature ranging from 382 to 419 °C. TG curves show a declined trend when the temperature falls below 382 °C. It is caused by the thermal decomposition of a small amount of copolymer modifier. The complete decomposition temperature of $Mg(OH)_2$ is 490 °C in theory, yet neither of the composites is decomposed completely after the temperature increases above 490 °C. It is due to the fact that a trace amount of heat-resistant decomposition products is mixed in the course of the experiment [13]. Thus, the copolymer film improved the dispersibility and compatibility of whiskers, yet it has little effect on thermal stability.

3.3 FTIR analysis of MH whiskers before and after modification

Figure 2 shows FTIR spectra of MH whiskers. Compared with unmodified whiskers, the significant decrease in –OH stretching vibration peaks at 3695 cm^{-1} and the sharper and wider absorption peak at 3434 cm^{-1} is attributed to the association of more –OH for modified MH whisker. The characteristic absorption peaks at 2962, 2869 and 1382 cm^{-1} are ascribed to the asymmetric vibration, symmetric vibration and symmetric deformation vibration of $–CH_3$, respectively. Moreover, the absorption peaks at 2915 and 2844 cm^{-1} are assigned to the asymmetric vibration and symmetric vibration of $–CH_2$. The sharp peak at 1729 cm^{-1} corresponds to C=O vibration of ester. The

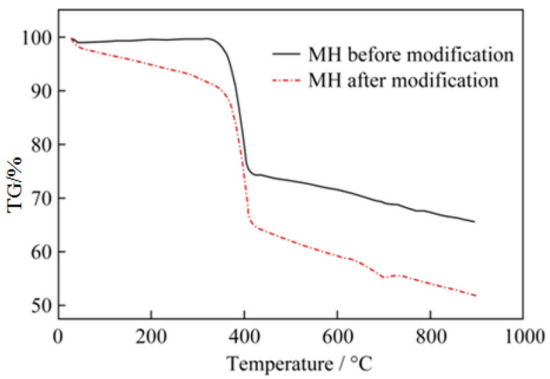

Fig. 1 TG spectra of MH whiskers before and after modification

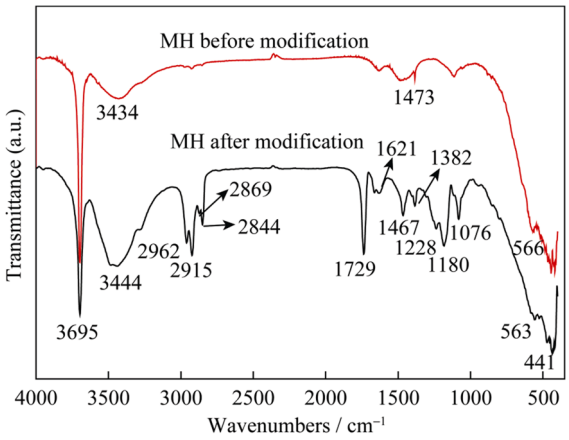

Fig. 2 FTIR spectra of MH whiskers before and after modification

small absorption peaks at 1621 and 1467 cm^{-1} are the asymmetric vibration and symmetric vibration of –COO–, respectively. The peaks at 1228 cm^{-1} are assigned to the stretching vibration of C–O of carboxylic acid. The peaks at 1180 and 1076 cm^{-1} are ascribed to C–O groups of the ester. Finally, the absorption peaks below 566 cm^{-1} are the stretching vibration of Mg.

Figure 2 provides the evidence for the existence of copolymers of n-butyl acrylate and maleic anhydride on the surface of modified MH whiskers. The coordination happens between carboxylate radical of copolymers and magnesium of MH whiskers, and the coordination pattern is affected by the location of antisymmetric and symmetric stretching vibration frequency of carboxylate radical. The frequency difference in the monodentate ligands is more than 200 cm^{-1}, while it is around 150 cm^{-1} for bridged coordination [14]. However, only slight differences exist among dozens of wavenumber in bidentate ligands. As seen in Fig. 2, the corresponding asymmetric vibration and symmetric vibration of stretching absorption peaks of –COO– are 1621 and 1467 cm^{-1}, respectively. The discrepancy of 154 cm^{-1} between them proves that bridged coordination is formed between magnesium and carboxylate radical.

3.4 XRD analysis of MH whiskers before and after modification

Figure 3 represents phase composition of MH whiskers before and after modification. It can be seen that the diffraction peaks of modified MH whiskers are consistent with the standard diffraction pattern of $Mg(OH)_2$, and no other peaks exist. It is illustrated that the crystals of modified MH whiskers do not change, and the purity remains at a high level [15]. However, compared with modified MH whiskers, for unmodified MH whiskers, the shape of the diffraction peaks is sharper and the intensity is

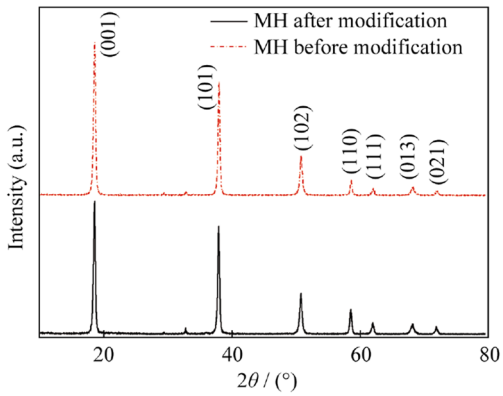

Fig. 3 XRD patterns of MH whiskers before and after modification

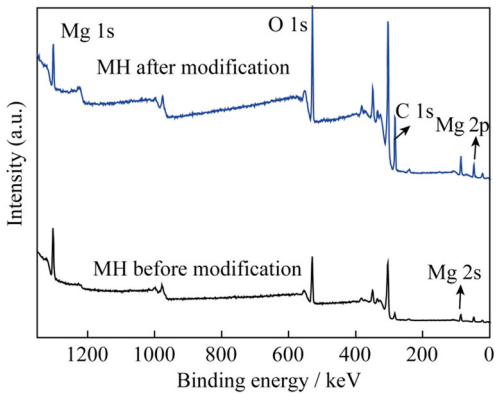

Fig. 5 XPS spectra for surface element analysis of MH whiskers before and after modification

slightly higher, indicating that the copolymer particulates on the surface of MH whiskers weaken the intensity of diffraction peaks and prevent agglomeration of whiskers.

3.5 Surface morphology of MH whiskers before and after modification

Figure 4a shows that the morphology of unmodified MH whiskers is straight, slim and easily agglomerated with smooth surface, while the modified MH whiskers are coated by spot and film-like material, as shown in Fig. 4b. It suggests that a copolymer layer made of n-butyl acrylate and maleic anhydride is generated [16]. The layer makes the surface of modified MH whiskers be rougher and improves the dispersion of whiskers significantly.

3.6 XPS analysis of MH whiskers before and after modification

Figure 5 shows that Mg and O are present on the surface of unmodified MH whiskers, while element C is found after modification. Comparisons of the spectra for MH whiskers before and after modification show that the peaks for elements C and O are significantly higher, suggesting that the copolymer containing element C is generated on the surface of whiskers after modification. It also confirms that the particulates in Fig. 1b are the copolymer of n-butyl acrylate and maleic anhydride. In order to further study the changes in the spectra for the elements, the peaks are dealt separately. The spectra for C 1s, O 1s and Mg 1s are obtained and analyzed, and the results are shown in Fig. 6.

As shown in Fig. 6a, Mg 1s binding energies of modified and unmodified MH whisker are, respectively, 1302 and 1303 eV, indicating that negative chemical displacement takes place and the electron cloud density of Mg atom increases after MH whiskers were modified. It is evident from Fig. 6b that no significant negative chemical displacements are found, while O 1s peak intensity of modified MH whisker is strengthened, which could be attributed to the layer generated on the surface of whiskers after modification. However, apparent C 1s spectra appearing in Fig. 6c could be found after modification, confirming the presence of organic layer on the surface of modified MH whisker. Moreover, the thickness of the layer is positively related to the peak intensity of elements [17]. Therefore, the thickness of the layer can be determined according to the peak intensity of elements. The peak intensity of C 1s spectra is very sharp after modification, demonstrating that C elements are adsorbed on the surface of modified MH

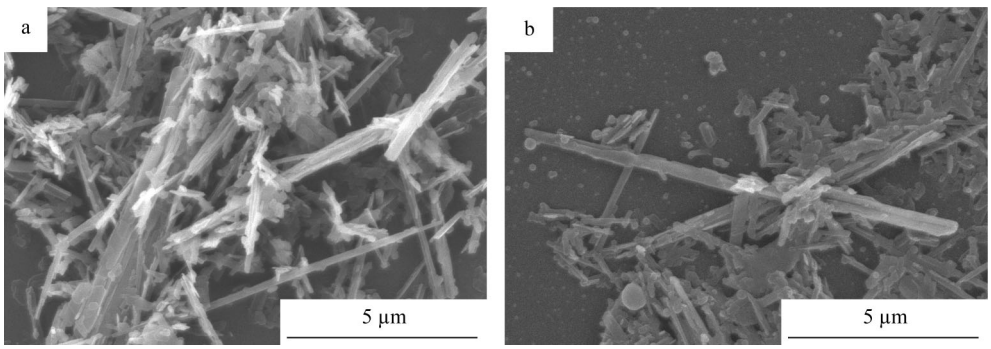

Fig. 4 SEM images of MH whiskers: **a** MH whiskers before modification and **b** MH whiskers after modification

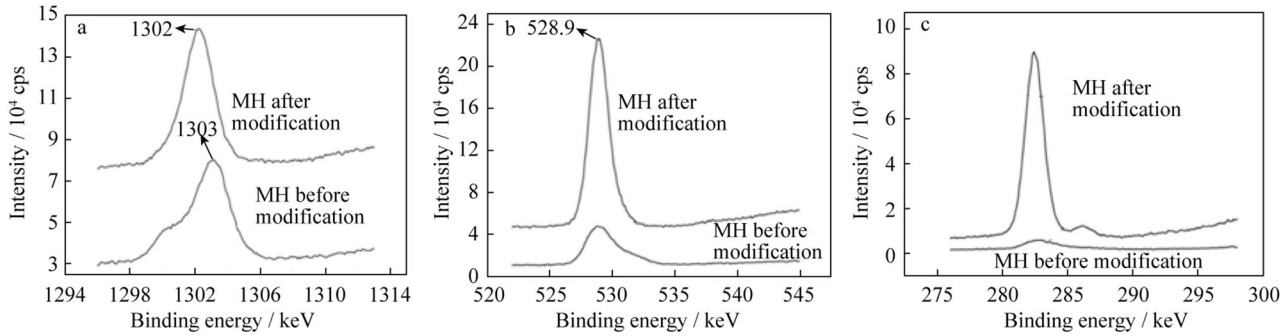

Fig. 6 XPS spectra for peak contrast of single element on MH whiskers before and after modification: **a** Mg 1s, **b** O 1s and **c** C 1s

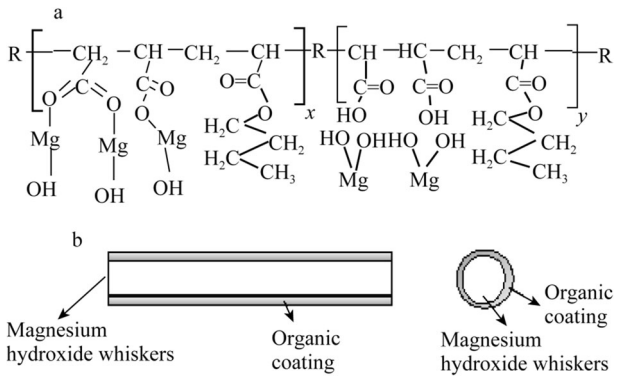

Fig. 7 MH whiskers modified via in situ copolymerization: **a** microstructure of organic coating and **b** macrostructure of modified magnesium hydroxide whiskers

whiskers. However, there are no C 1s spectra in unmodified MH whiskers.

3.7 Surface molecular model of modified MH whiskers

Based on FTIR, SEM and XPS analysis, the surface molecular model of MH whiskers modified via in situ copolymerization can be demonstrated.

In Fig. 7, the polymerizable small molecule monomers are coordinated with magnesium ions and hydroxyl on the surface of MH whiskers. While the initiator was added to micro-emulsion, the small molecule monomers are copolymerized and an organic coating is formed on the surface of MH whiskers. The formation of the copolymer can be verified by FTIR analysis of functional groups. Meanwhile, the thickness of copolymers could be determined by the peak height of C 1s spectra on the surface of modified MH whiskers. Based on the results of the analysis, the structure model of modified MH whiskers is established, which is consistent with the functional group analysis and elemental analysis, and this confirms the rationality and accuracy of the structure model.

4 Conclusion

MH whiskers were modified successfully via in situ copolymerization of n-butyl acrylate and maleic anhydride. The contact angle and activation index of modified MH whiskers are, respectively, 105° and 76.5%. The thermal stability of MH whiskers decreases slightly due to the existence of the copolymer, but the compatibility of whiskers in the organic phase is improved significantly after modification. SEM and XRD results show that a lot of copolymer particulates are generated on the surface of MH whiskers, which makes it rough and weakens the intensity of diffraction peaks. According to XPS analysis, the decrease in binding energy of Mg element induced the negative chemical displacement, and the modifier molecular is coordinated with Mg element on the surface of MH whiskers. Based on analysis results, the surface molecular model of MH whiskers modified via in situ copolymerization of n-butyl acrylate and maleic anhydride is established.

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